

METHOD 43

DETERMINATION OF VOLATILE METHYLSILOXANES IN SOLVENT BASED COATINGS, INKS AND RELATED MATERIALS

REF:	Regs:	8-3	8-19	8-32	
			8-4	8-20	8-38
			8-11	8-23	8-43
			8-12	8-26	8-45
			8-13	8-29	8-51
			8-14	8-31	

1) PRINCIPLE

~~1.1 The U. S. Environmental Protection Agency has excluded **volatile methysiloxanes (VMS)** from the list of Volatile Organic Compounds.~~

1.1 This method is applicable to the determination of the following volatile methylsiloxanes (VMS) in solvent based coatings, inks and related products:

hexamethyldisiloxane	octamethyltrisiloxane
decamethyltetrasiloxane	decamethylcyclopentasiloxane
octamethylcyclotetrasiloxane	

1.2 The concentration of the VMS is determined by gas chromatography using n-octane, or any appropriate compound, as the internal standard.

1.3 The established concentration range for this method is 10% to 65%. There is no reason to believe that it will not work outside this range. The upper limit of the range can be extended by lowering the sample weight.

1.4 Aliphatic hydrocarbons may interfere in the analysis of the VMS compounds.

1.5 This method may not be applicable to all types of coatings, inks or related materials.

2) APPARATUS

- 2.1 Gas Chromatograph.** This unit is fitted with a flame ionization detector (FID), a ~~glass-sleeve~~ liquid injection port with glass insert, a temperature programmer and a compatible integrator or data station. The recommended operating parameters are as follows:

	<u>Initial</u>	<u>Final</u>
Oven Temperature (°C)	50	210
Time Delay (Min)	5	5
Temperature Program Rate (°C/min)	6	
Injector Temperature (°C)	250	
Detector Temperature (°C)	250	
Carrier Gas	He	
Carrier Gas Flow (cm/sec)	30	
Injection Sample Size (µl)	1	

- 2.2 Analytical Column.** Any analytical column capable of separating and resolving the compounds of interest is acceptable. The recommended analytical column is:

2.2.1 A 60 m x 0.32mm I.D., 1.0 micron film thickness, DB-1 Column (J & W Scientific). ~~This column is available from J&W Scientific, 91 Blue Ravine Road, Folsom, CA 95630-9928.~~

- 2.3 Micro Syringe, 10 µl.**

- 2.4 Burrell Wrist Action Shaker**

- 2.5 Analytical Balance.** Capable of weighing to ± 0.0001 g

- 2.6 Disposable Transfer Pipets. Beral Pipettes.** 3ml with 1 and 2 ml graduations. These are available from Curtin Matheson, Company ~~(Catalog #376-970).~~

- 2.7 Spatula.**

- 2.8 Vials** with screw caps. 3 dram size.

- 6.1 Eberbach Shaker.**

- 2.10 Red Devil Paint Shaker** for gallon size containers.

2.11 Disposable Syringe. 3-5 cc used for coatings with highly volatile solvents.

3) REAGENTS

3.1 Carbon Disulfide (CS₂), low benzene (<1ppm) or other suitable solvent, reagent grade.

3.2 n-Octane, or other suitable internal standard, Reagent grade, 99 + % purity.

3.3 Volatile Methylsiloxanes (VMS) as listed in Section 1.2, Reagent Grade or highest available purity.

3.4 Helium or Nitrogen Cylinder, 99.995% Purity or Higher.

3.5 Hydrogen Cylinder or Hydrogen Generator.

4) ANALYTICAL PROCEDURE

4.1 Determination of % Total Volatiles of the Coating.

4.1.1 Mix the coating thoroughly for about 30 minutes, using an Eberbach or Red Devil Paint Shaker. It is essential that the samples be well mixed to obtain valid results. Stirring with a spatula may also be required.

4.1.2 To determine the % total volatiles, refer to **Method 22, Sections 4.1 and 4.2.**

4.2 Determination of Density of the Coating. To determine the density, refer to **Method 22, Section 4.3.**

4.3 Determination of VMS ~~Volatile Methylsiloxane~~ Content of the Coating by Gas Chromatography.

4.3.1 Set up the gas chromatograph as described in **Section 2.1.**

4.3.2 Screen the sample for the presence of peaks interfering with the internal standard.

- 4.3.2.1** Prepare a solution of n-octane in CS₂ by weighing 0.1 g (± 0.0001 g) of n-octane into a pre-weighed sample vial. Add 8 ml of CS₂, cap the vial and mix the solution thoroughly. (**Note 1**)

NOTE 1: CS₂ is flammable. It is harmful if inhaled or absorbed through the skin. It is a possible mutagen/teratogen. Use only with adequate ventilation. Avoid contact with skin, eyes and clothing. If the material to be analyzed is not compatible with CS₂, use a different solvent such as dimethylformamide or tetrahydrofuran.

- 4.3.2.2** Inject a 1 μ l aliquot of the solution (**4.3.2.1**) into the gas chromatograph. Retain the chromatogram.
- 4.3.2.3** Weigh 0.3 g (± 0.0001 g) of the mixed coating (**4.1.1**) into a pre-weighed sample vial. Add 8 ml of CS₂. Cap the vial, mix thoroughly and allow to stand for about 5 minutes. Inject a 1 μ l aliquot of the mixture into the gas chromatograph. Compare the sample chromatogram to that obtained in **Section 4.3.2.2**. If there is no peak that interferes with octane in the sample chromatogram, then proceed to **Section 4.3.3**. If an interfering peak is found use another appropriate solvent as internal standard.

4.3.3 Determination of Response Factor (R_{vms}) for the Volatile Methylsiloxane.

- 4.3.3.1** Inject 1 μ l of CS₂ into the gas chromatograph to check for contamination. If it is contaminated, open a fresh bottle and repeat the step.
- 4.3.3.2** Weigh accurately 0.1 g (± 0.0001 g) of the VMS and 0.1 g (± 0.0001 g) of n-octane a pre-weighed sample vial. Add 8 ml of CS₂. Cap and shake the vial contents thoroughly for 15 minutes, using the Burrell Wrist Action Shaker.
- 4.3.3.3** Using a 10 μ l syringe, inject separately 1 μ l of the mixture (**4.3.3.2**) into the gas chromatograph. Integrate and record the peak areas of n-octane and the VMS. Retain the chromatogram. The order of elution is ~~carbon disulfide~~ CS₂, n-octane and VMS. (**See Figure 1**).

4.4 Calculation for the Response Factor, R_{VMS} , of the Individual VMS ~~Volatile~~ **Methylsiloxane.**

4.4.1 Calculate the response factor, R_{VMS} of each VMS to the internal standard by means of the following equation: **(NOTE 2)**

$$4.4.1.1 \quad R_{VMS} = \frac{W_i \times A_{VMS}}{W_{VMS} \times A_i}$$

Where:

- W_i = The Weight of the internal standard, g.
- W_{VMS} = The Weight of VMS, g.
- A_{VMS} = The Peak area of VMS.
- A_i = The Peak area of the internal standard.

NOTE 2

4.5 Gas Chromatographic Determination of the VMS ~~Volatile Methylsiloxane~~ Content of the Coating.

4.5.1 Weigh accurately 0.2 to 0.5 g (± 0.0001 g) of the mixed coating **(4.1.1)** and 0.1 g of n-octane in a pre-weighed sample vial. Add 8 ml of CS_2 . Immediately cap the vial.

4.5.2 Shake the mixture on a Burrell Wrist Action Shaker for 15 minutes. It is essential that the sample be thoroughly mixed. Allow the sample to stand undisturbed for about 5 minutes prior to injection. This is to allow the solids to settle at the bottom of the vial.

4.5.3 Inject a 1 μ l aliquot of the supernatant liquid from **(4.5.2)** into the gas chromatograph. The areas of the VMS and the octane peaks are integrated and recorded. Retain the chromatogram.

4.6 Calculation for % VMS ~~Volatile Methylsiloxane~~ in the Coating.

4.6.1 Using the data obtained in **(4.5.3)**, calculate the weight % of each VMS in the sample, as follows:

$$4.6.1.1 \quad \% \text{ VMS (w/w)} = \frac{A_{VMS} \times W_i}{A_i \times W_s \times R_{VMS}} \times 100$$

Where:

A_{VMS} = Area of the VMS peak.

A_i = Area of the internal standard peak.

W_i = Weight of the internal standard, g.

W_s = Weight of the coating sample, g.

R_{VMS} = The Response factor for VMS.

4.6.2 Run the analysis in duplicate. Reanalyze the sample if the results vary by more than $\pm 1\%$ (absolute) from the mean.

5) CALCULATION FOR COMPLIANCE OF COATING CONTAINING VMS VOLATILE METHYLSILOXANES

5.1 Weight (g) of Total Volatiles /l of Coating = $1000 \text{ ml/l} \times D \times TV \times 10^{-2}$

Where: D = Density of Coating (4.2), g/ml.

TV = % Total Volatiles in the Coating (4.1.2), w/w.

5.2 Weight (g) of VMS /l of Coating = $1000 \text{ ml/l} \times D \times (4.6.1.1) \times 10^{-2}$

Where: D = Density of Coating, g/ml.

(4.6.1.1) = % VMS (W/W) in the Coating

5.3 Total Weight (g) of VMS per liter /l of Coating = Sum of the Individual Weights in grams of VMS in 1 liter of Coating (5.2).

5.4 Volume (ml) of VMS/l Coating = $\frac{(5.2)}{D_{VMS}}$

Where: D_{VMS} = 0.760 for hexamethydisiloxane

0.810 for octamethyltrisiloxane

0.850 for decamethyltetrasiloxane

0.950 for octamethylcyclotetrasiloxane

0.950 for decamethylcyclopentasiloxane

5.5 Total Volume of VMS /l of Coating = Sum of the Individual Volumes (ml) of VMS in 1 liter of Coating (5.4).

5.6 Grams VOC/l Coating (less VMS) = $\frac{[(5.1) - (5.3)]}{1000 \text{ ml/l}}$

$$5.7 \text{ lb VOC/gal Coating (less VMS)} = \frac{[1000 \text{ ml/l} - (5.5)]}{(5.6) \times 8.34 \times 10^{-3}}$$

$$\text{Where: } 8.34 \times 10^{-3} = \frac{3.785 \text{ l/gal}}{454 \text{ g/lb}}$$

5.8 For low solid materials, where VMS is considered part of the coating.

$$5.8.1 \text{ Grams VOC/l Coating} = [(5.1) - (5.3)]$$

$$5.8.2 \text{ lb VOC/gal Coating} = (5.8.1) \times 8.34 \times 10^{-3}$$

6) REFERENCES

~~6.1 Hollis, O.L., "Separation of Gaseous Mixtures using Porous Aromatic Polymer Beads", Anal. Chem. 38, 309, 1966.~~

6.1 **"Volatile Content of Paint" "Standard Test Method for Volatile Content of Coatings"**, ASTM Designation D2369-93 95, Book of ASTM Standards Annual Book of ASTM Standards, Vol. 06.01, 1995.

~~6.2 Density of Paint, Varnish, Lacquer and Related Products" "Standard Test Method for Density of Liquid Coatings, Inks, and Related Products"~~, ASTM Designation D1475-90, Annual Book of ASTM Standards, Vol. 06.01, 1993.

~~6.3 "Determination of Water Content of Water Reducible Paints by Direct Injection into a Gas Chromatography", ASTM Method D3792-91, Book of ASTM Standards~~

6.3 **"Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph"**, ASTM Method D4457-85 (Reapproved 1991), Book of ASTM Standards, Vol. 06.01, 1993.

6.4 **"BAAQMD Manual of Procedures,"** Vol.3, Method 22.

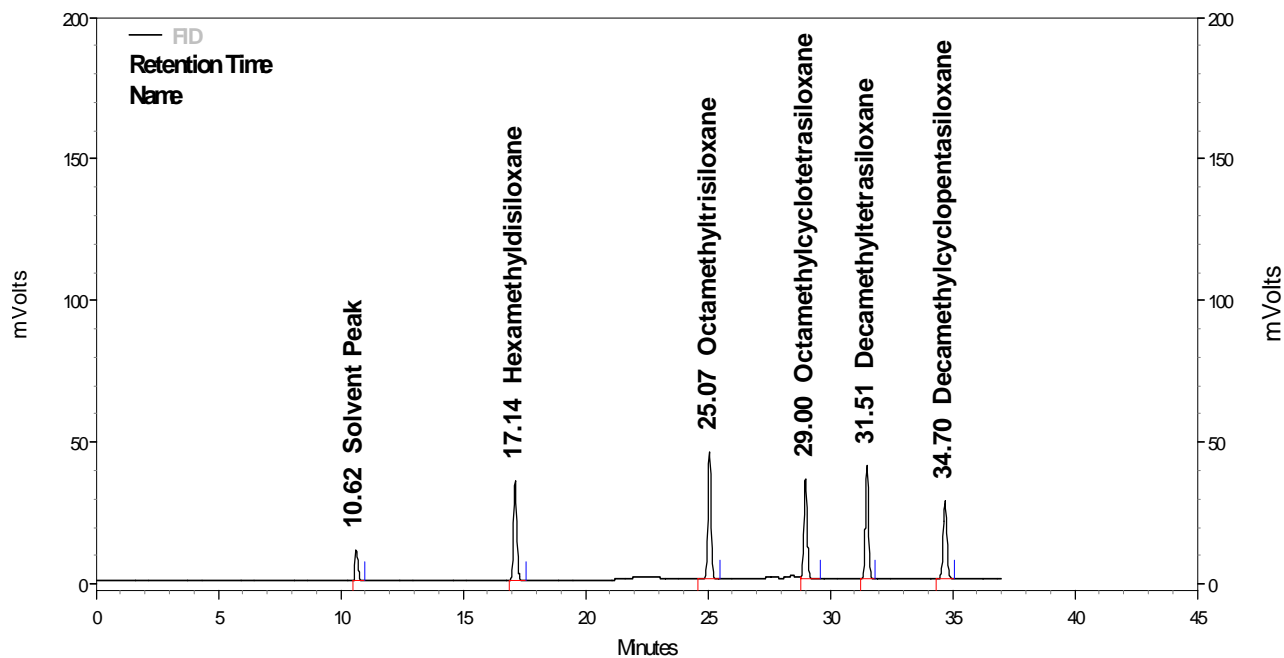


FIGURE I

A TYPICAL CHROMATOGRAM SHOWING THE VOLATILE METHYSILOXANE PEAKS